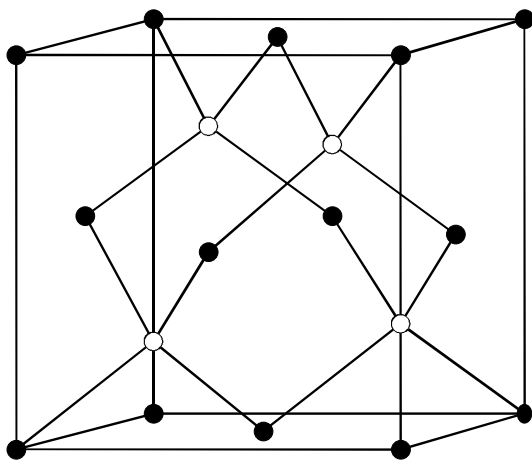


## Material Science of Carbon

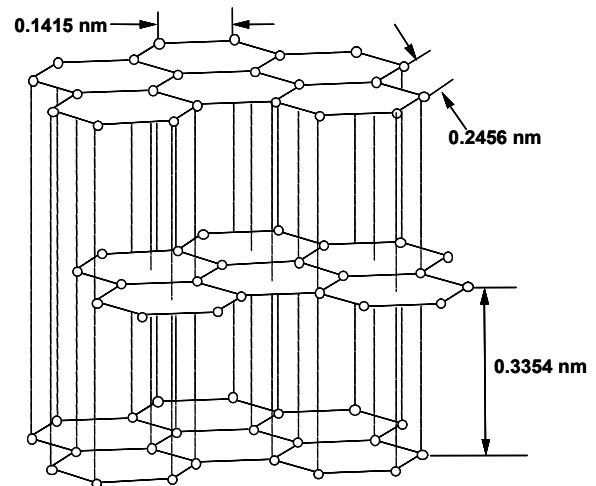
Carbon is a ubiquitous material that is essential for the functioning of modern society. Because carbon can exist in a multitude of forms, it can be tailored to possess practically any property that might be required for a specific application. The list of applications is very extensive and includes: aircraft brakes, electrodes, high temperature molds, rocket nozzles and exit cones, tires, ink, nuclear reactors and fuel particles, filters, prosthetics, batteries and fuel cells, airplanes, and sporting equipment.

The different forms of carbon arise from the fact that carbon exists in three very different crystalline forms (allotropes) with a variety of crystallite sizes, different degrees of purity and density, as well as various degrees of crystalline perfection. These allotropes are possible because carbon has four valence electrons and is able to form different kinds of bonds with other carbon atoms.

For example, diamond with a covalently-bonded face-centered cubic structure can exist as a naturally-formed single crystal as large as 200 g. Diamond, the hardest material known to man, is also able to be made synthetically by a variety of processes. For example, high pressure anvils can be utilized to produce relatively small single crystals while a vapor-phase process such as chemical vapor deposition (CVD) is employed to deposit crystalline and amorphous coatings having grain sizes on the micron scale, and a variety of degrees of crystallite orientations. Synthetic diamonds in all forms are used as hard scratch-resistant coatings and tool coatings for grinding, cutting, drilling and wire drawing. Other applications include heat sinks and optical windows among others.



Diamond Structure



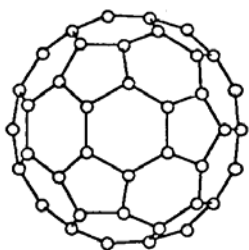
Hexagonal Graphite Structure

The most abundant forms of carbon exist as various forms of the allotrope hexagonal graphite. The perfect crystalline structure of graphite is a hexagonal layered structure in which the atoms in each layer are covalently-bonded while the graphene layers are held together by weaker Van Der Waals forces. This difference in bonding is what is

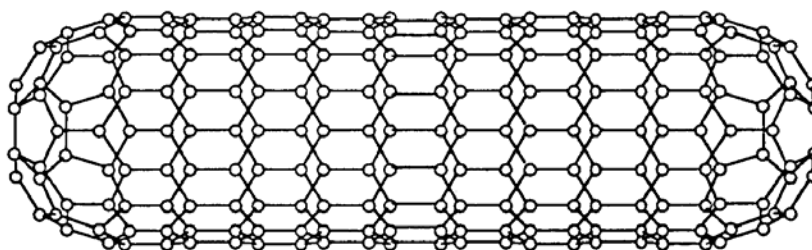
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responsible for the great anisotropy in mechanical, thermal, electrical and electronic properties.

With the relatively recent discovery of the nano-forms of carbon in the last two decades, the range of properties that carbon can possess and the gamut of potential applications has greatly increased. The linear portions of these molecules are simply rolled up graphene layers, while the curved portions consist of graphite hexagons in contact with pentagons. Although commercial applications for both bucky balls and carbon nanotubes are not well defined at the time of this writing, the high aspect ratio of nanotubes, along with the fact that they are stronger ( 63 GPa ) and stiffer (~1000 GPa ) than any other known material, means that the potential for these materials is great.



**BUCKYBALL**



**NANOTUBE**

Adding to the complexity of understanding and modeling carbon is the fact that, in its various forms, it rarely exists in a perfect single crystalline state. For example, perfect graphitic structure only exists in the various forms of natural graphite flakes and graphitizable carbons, which are carbons formed from a gas or liquid phase process. An example of a graphitizable carbon would be highly oriented pyrolytic graphite (HOPG), which is formed by depositing one atom at a time on a surface utilizing the pyrolysis of a hydrocarbon, such as methane or propylene. This deposited material is then graphitized employing both thermal and mechanical stress.

In the overwhelming number of applications, single crystal graphite is not employed. Rather a carbon with some degree of graphite structure is utilized. Excluding crystallite imperfection, such as vacancies, interstitials, substitutions, twin planes, etc., the form of carbon that most closely approaches single crystal graphite is turbostratic graphite. This form of carbon looks very similar to graphite except that, although there may be some degree of perfection within the planes, the adjacent planes are out of registry with one another. That is, in the hexagonal graphite structure, there is an atom in each adjacent plane that sits directly over the center of the hexagonal ring. In turbostratic graphite, the adjacent planes are shifted with respect to one another and are out of registry. This results in an increase in the interlayer spacing, which can increase from 0.3354 nm to more than 0.345 nm. If the value exceeds this, the structure exfoliates. Heating to temperatures in excess of 2800 K provides energy for mobility and can convert turbostratic graphite to single crystal graphite in a process called graphitization.

As stated above, a carbon material that goes through either a gas phase or liquid phase process in its conversion to carbon (carbonization process) can be converted to a graphitic structure employing time and temperature in the range from 2000-2800 K. This means that materials formed in the gas phase (like carbon black and pyrolytic carbon) can be converted to a graphitic structure. Cokes and carbon fibers fabricated from petroleum, coal tar, or mesophase pitch are also graphitizable. On the other hand, chars formed directly from organic materials, such as wood and bone used for activated carbon, PAN fibers formed from polyacrylonitrile, and vitreous carbons formed from polymers, such as phenolic or phenyl-formaldehyde, are amorphous and not graphitizable because they maintain the same rigid non-aligned structure that they possessed before carbonization.

In addition to the degree of crystalline order, the properties of carbons are also determined by the crystallite size and orientation of polycrystalline carbons. The largest carbon parts that are manufactured are electrodes for the steel and aluminum industries. These electrodes can weigh more than 3 tons and are fabricated by extruding a mixture of fine petroleum coke and coal tar pitch. The extrusion process causes some preferential alignment of the crystallites, and baking to 2800 K produces a polycrystalline graphite part that has high strength and conductivity. To make isotropic graphite, fine-grain coke and petroleum pitch are isostatically pressed.

By proper selection of precursor material and processing condition, a carbon with practically any property can be produced. For example carbons can be hard (chars) or soft (blacks), strong (PAN fibers) or weak (aerogel), stiff (pitch fibers) or flexible (Graphoil®), as well as anisotropic (HOPG) or isotropic (polycrystalline graphite). In addition, porosity, lubricity, hydrophobicity, hydrophilicity, thermal conductivity and surface area can be varied over a wide range. For example, surface area can vary from 0.5 m<sup>2</sup>/g for a fiber to > 2000 m<sup>2</sup>/g for an activated carbon, while thermal conductivity can range from 0.001 W/(m-K) for an amorphous carbon foam to 1100 W/(m-K) for a pitch fiber, and 3000 W/(m-K) for diamond.

Carbon materials have been studied and produced for thousands of years. (The Chinese used lampblack 5000 years ago.) While much is understood about carbon, there are some very important areas in which there is still a lack of understanding. These areas fall generally into the production of graphitic material and the oxidation protection of carbon and graphite materials. A better understanding of the science of carbon formation will allow increased performance at reduced cost, while effective oxidation protection at ultra high temperature will enable a whole range of new technology.

Currently, the highest performance and highest cost form of carbon are carbon-carbon composites, which are truly a unique class of materials. These composites, which are stronger and stiffer than steel as well as being lighter than aluminum, are currently used principally in high performance-high value applications in the aerospace and astronautics industries. The highest volume of carbon-carbon is used as brake rotors and stators for military and commercial aircraft because it has high thermal conductivity, good frictional properties, and low wear. Astronautic applications include, rocket nozzles, exit cones,

and nose tips for solid rocket boosters as well as leading edges and engine inlets for hypersonic vehicles. In these applications carbon-carbon's high strength and stiffness as well as its thermal shock resistant are keys to its success. For re-useable hypersonic vehicles, the fact that carbon does not go through phase changes like some ceramics and in fact its mechanical properties actually increase with temperature make this a very valuable material. For satellite applications carbon-carbon's high specific strength and stiffness as well as its near zero thermal expansion make it an ideal material for large structures that require dimensional stability as they circle the earth.

Carbon-carbon composites are fabricated through a multi-step process. First, carbon fibers, which carry the mechanical load, are woven, braided, felted, or filament wound into a preform which has the shape of the desired part. The preform is then densified with a carbon matrix, which fills the space between the fibers and distributes the load among the fibers.

It is this densification process that is not well understood. Unlike the manufacture of fiberglass, in the formation of carbon-carbon composites the matrix precursor is not just cured but must be converted into carbon. The conversion of polymers to produce a char, as well as the conversion of a hydrocarbon gas to produce a graphitizable matrix, is fairly well understood. What is not clear is the process of converting a pitch-based material to a high quality graphitizable matrix. That is, for example, starting with a petroleum or coal tar pitch, heat soaking converts this isotropic mixture of polyaromatics into anisotropic liquid crystalline spherical droplets called mesophase spherules. These spherules ultimately coalesce to form a continuous second phase which ultimately pyrolyzes to form a graphitic structure. Although this process has been observed microscopically, little is known about the process, or even exactly what mesophase is or what molecular precursors are needed to form mesophase. Little is known because it has proved impossible to accurately analyze mesophase precursors, mesophase itself, or the intermediates between mesophase and graphite. What is needed is a model that can predict the growth of single aromatic rings through the mesophase intermediate and into an ordered graphitic structure.

Moreover, it is well known that during pyrolysis, mesophase converts into a matrix that is very anisotropic. The formation of onion-like "sheaths" takes place on the surface of individual carbon fibers in the carbon composite. As these sheaths grow outward from the fiber surfaces, they ultimately collide, forming point defects called disclinations. This behavior has a pronounced effect on both the chemical and physical properties of the carbon-carbon composite. A model that describes this matrix contribution to the composite's properties would be of great benefit for understanding experimental data, such as thermal conductivity and mechanical properties, as well as for prediction of composite behavior.

Although carbon-carbon composites possess high strength, stiffness, and thermal shock resistance, making them an excellent high temperature structural material, their Achilles heel is oxidation. Above 670 K, carbon oxidizes. This means that if it is unprotected, it cannot be used for long-term high temperature applications. Today it is used for short-

term applications, such as aircraft brakes, as well as rocket nozzles, exit cone, and nose tips. To be used in long-term applications such as reusable hypersonic vehicles, it must be protected. Currently, an adequate protection system at ultra high temperatures ( $>2700$  K) does not exist. There is a tremendous need and payoff for a non-structural barrier that can keep oxygen from reaching a carbon surface at 2700 K. Efforts to fabricate these coatings have been unsuccessful. What is probably required for success is some sort of novel functionally graded coating which will require modeling material properties as well as thermal stresses.

Finally, the rather recent discovery of Buckyballs and nanotubes, which are three-dimensional analogs of hexagonal graphite, has also rekindled the need for models of the intercalation of graphite. This process occurs when various elements, such as lithium, sodium, or bromine, "sandwich" themselves between graphene planes. This greatly alters the thermal and electrical properties of the graphite. Similar behavior is beginning to be demonstrated in Buckyballs and nanotubes. The need for models based on computational chemistry would be of great help in this area.

For additional information on carbon, there are many good reference works. Most focus on specific forms of carbon such as carbon blacks, active carbons, fiber, composites, intercalation compounds, nuclear graphites, etc. For general topics the handbook by Pierson (Pierson, 1993) is a good text. A reference work covering scores of subjects in great detail is the 28 Volume Chemistry and Physics of Carbon (Radovic, 2001) which has had three Editors over the last 39 years.

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